

Monitoring Chemical Reactions

with Terahertz Rotational Spectroscopy

Supplementary Information

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Table of Contents

Materials and Methods (pp. S2-S5)

Supplementary Figures (pp. S6-S10)

Fig S1 – External and Internal Calibrations for OCS and CO

Fig S2 – Reaction chamber diagram

Fig S3 – Electronics diagram for the experimental apparatus

Fig S4 – Extinction Spectrum of AlNCs

Fig S5 – CO/OCS/H₂S adsorption in an empty chamber

Fig S6 – Influence of pretreatment temperature on AlNC surface chemistry

Fig S7 – Multiple OCS Isotopologue Transitions

References (p. S10)

Methods/Materials

Vacuum Chamber

The reaction chamber is a standard CF 5-Way cross (Kurt Lesker, 2¾ inch tube diameter), with quartz viewports on the four in-plane flanges. The 5th arm is adapted down to a series of 1.5 inch KF components (Kurt Lesker). An MKS Baratron pressure gauge (0.1 Torr, MKS 627F) was used to monitor the pressure at various parts of the system. A scroll pump-turbo pump (ScrollVac SC 5D, Pfeiffer HiPace 300) system is used to evacuate the system (base pressure < 10⁻⁵ Torr). The horizontal arm of the chamber is used as a waveguide for the microwave radiation, while the vertical arm is utilized for optical illumination of the catalyst sample.

Catalyst Heating Stage

A custom stage was built in order to hold the catalyst material, while integrating heating and thermocouple capabilities. A 2.25" OD CF flange was equipped with four feed-throughs: (1) 0.25" Cu tube, (2) Type-K thermocouple connection, and (3) Electrical connections of 0.05" Cu wire rated for 5kV and 15A. An Al block was milled to be supported via the 0.25" Cu tube, accept a UHV cartridge heater, and support the catalyst via a fine mesh screen contained within a 5 mm OD stainless steel ring. The UHV substrate heater rated to 1200 °C (TB-175; HeatWave Labs, Inc.) was connected to both leads of the 0.05" Cu wires and secured firmly inside the underside of the Al block using small screws. The K-type thermocouple was positioned as close as possible to the catalyst to measure surface temperatures accurately.

Microwave oscillator

A narrowband tunable microwave synthesizer followed by three-frequency multipliers (VDI, x18) produces radiation in the frequency band from 210-330 GHz. The signal is detected by a zero-biased Schottky diode (VDI) operating in this band. The signal is passed to a transimpedance amplifier (Perry Instruments), then a low noise preamplifier (SRS SR560) and a lock-in amplifier (AMETek Lock-in Amplifier 7270 DSP). The output is digitized (NI USB-6251 M Series).

Aluminum Nanocrystals

The aluminum nanocrystals were synthesized using a published protocol where size control is achieved by varying volume fractions of THF and 1,4-dioxane.¹ All solvents and reagents were purchased from Sigma-Aldrich and dried and distilled under inert atmosphere before use. Tetrahydrofuran (THF) and 1,4-dioxane were added to a dry Schlenk flask under Ar atmosphere, and the flask was heated in a 40°C oil bath. After approximately five minutes, 6.5 mL of 0.5 M N,N- dimethylethylamine alane was added. After two minutes 0.5 mL of a 3.3 mM solution of titanium (IV) isopropoxide in toluene was added rapidly via syringe. After 24 hours, the AINCs were isolated by centrifugation and suspended in 2-propanol until used.

Catalyst Preparation

AINCs were supported on at 10 wt% loading on acid washed and calcined SiO₂ with a particle size distribution between 0.5 – 10 µm and 80% between 1-5 µm (Sigma-Aldrich). A known weight of SiO₂ was placed into a centrifuge tube, followed by the addition of an ~ 1g/L solution of AINCs suspended in 2-propanol. Exact volumes and weights are adjustable, but 10 wt% loading was used in the experiments described here. The AINC/SiO₂ mixture was sonicated for ~5 minutes before centrifuging at 500G to isolate the solid. Excess 2-propanol was decanted and the remaining solid was dried under vacuum before loading into the spectrometer.

Calibration for Quantitative Analysis

As mentioned above, this method relies on accurate measurements of the unmodulated integrated transition line strengths, and the challenge is to extract these from the measured modulated line shapes. To do this, an accurate numerical fit of the modulated line shape is required, from which the amplitude, center frequency, and linewidth of the unmodulated Voigt line shape may be extracted and the integrated line strength may be calculated. These amplitudes must then be converted from voltage measured by the detector to fractional absorption of the transmitted power through the chamber. However, quantitative measurements of the absorption strength are difficult to obtain for many reasons, including the uncertainty of the detected power and its relation to the measured voltage from the detector, its sensitivity to alignment, and the commensurately strong frequency-dependent power variations mentioned above. To overcome these limitations, a calibration of the absorption strength for a given experimental configuration must be performed. Because the absorption coefficient of rotational transitions can be calculated precisely,^{2,3} and because the effect of the modulation is understood, what is needed is a means to correlate this calculated line strength with the measured line strength.

These calibrations are most easily performed in the low pressure, Doppler broadened regime where the signal amplitude grows linearly with molecular concentration (and with pressure defined by the ideal gas law) and Gaussian line shapes may be used. The first step is to measure the strength of the absorption feature for a rotational transition of a reference gas as a function of pressure. For example, in Fig. S1a and S1b we plot the integrated line strengths of known pressures of OCS and CO, respectively, between 0 – 100 mTorr. The slope of the calibration curves is found by simply applying a linear fit with a zero-intercept, and by utilizing the known ratios of transition intensities of molecular species of interest, these external

calibrations can be applied to gases of unknown composition. This approach effectively allows us to calculate concentrations of gases for which a calibration has not previously been done.

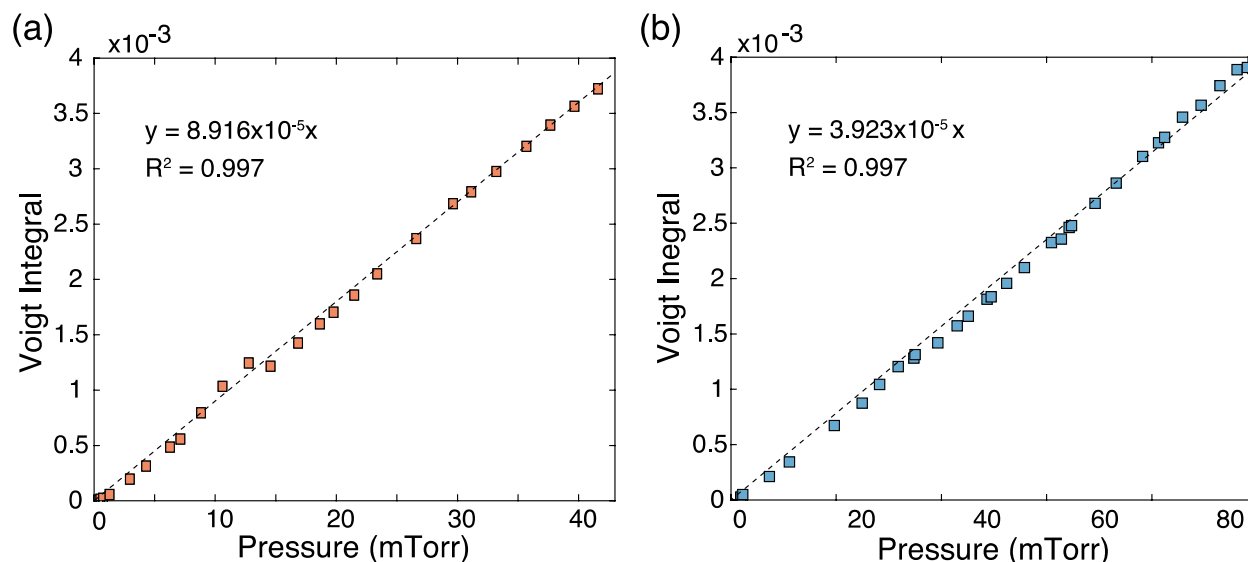


Figure S1. External Calibrations of (a) OCS and (b) CO. Black curves represent the linear fit with a $y=0$ intercept. Measured pressures were recorded on a Baratron pressure gauge.

Limits of Detection

Based on the slopes obtained from individual external calibrations, the limits of detection can be estimated based on the signal to noise ratio (SNR) of individual transitions. The transition amplitude is obtained by fitting the integrated Voigt profile, described above, while the standard deviation of the noise is obtained by a simple linear regression analysis of the modulated baseline. By extrapolating the SNR of an external calibration to an SNR value equal to 1, an estimated limit of detection (LOD) for an individual gas can be obtained. Based on the same principles exploited for the quantitative calibrations described above, a simple ratio of the transition frequencies intensity of an unknown chemical species can allow extrapolation of its theoretical detection limit.

Supplementary Figures

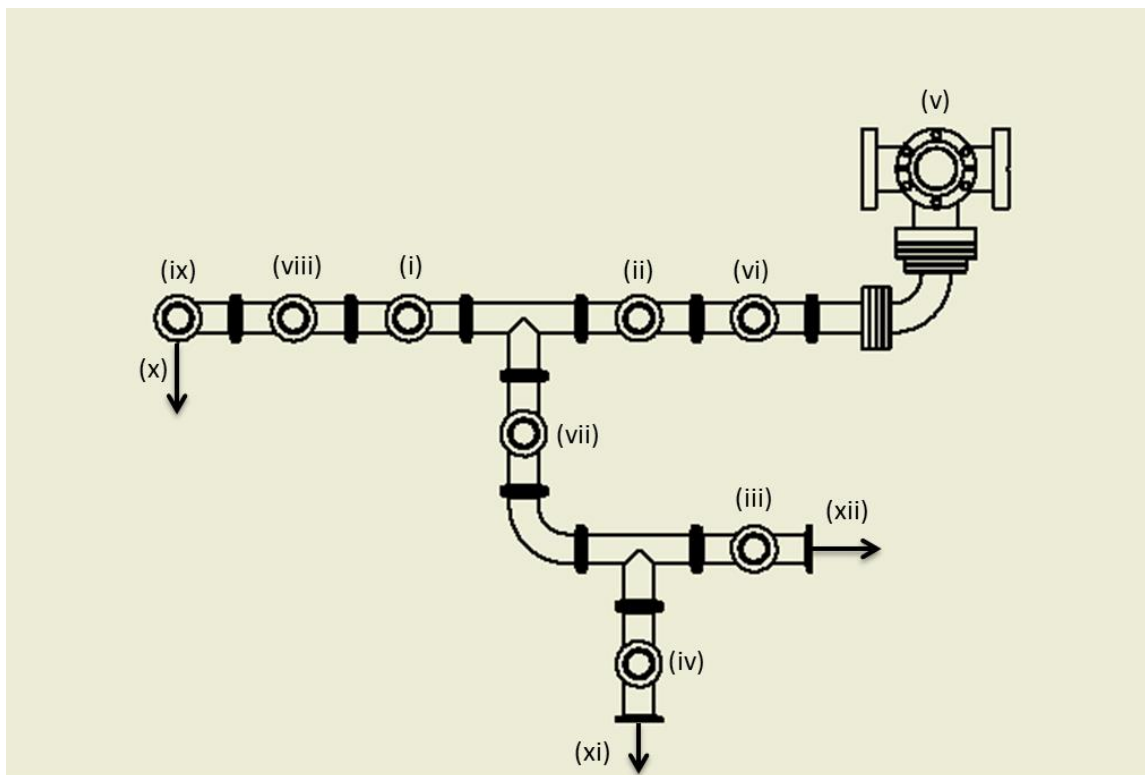


Figure S2. Full experimental apparatus diagram. (i), (ii), (iii), (iv) are VAT valves used to isolate individual sections of the reaction chamber. (v) Reaction chamber as detailed in main text Fig. 1a. (vi) Baratron pressure gauge capable of measurements between 0-100 mTorr. (vii) convection pressure gauge capable of measuring pressures between 0-760 Torr. (viii) Ion gauge for measure vacuum baselines. (ix) Isolation valve for (x) vacuum manifold. (xi) To inert gas (N_2 , He, or Ar) to bring chamber to atmosphere when changing the catalyst or doing maintenance. (xii) To gas inlet delivery ($OCS/CO/H_2S$)

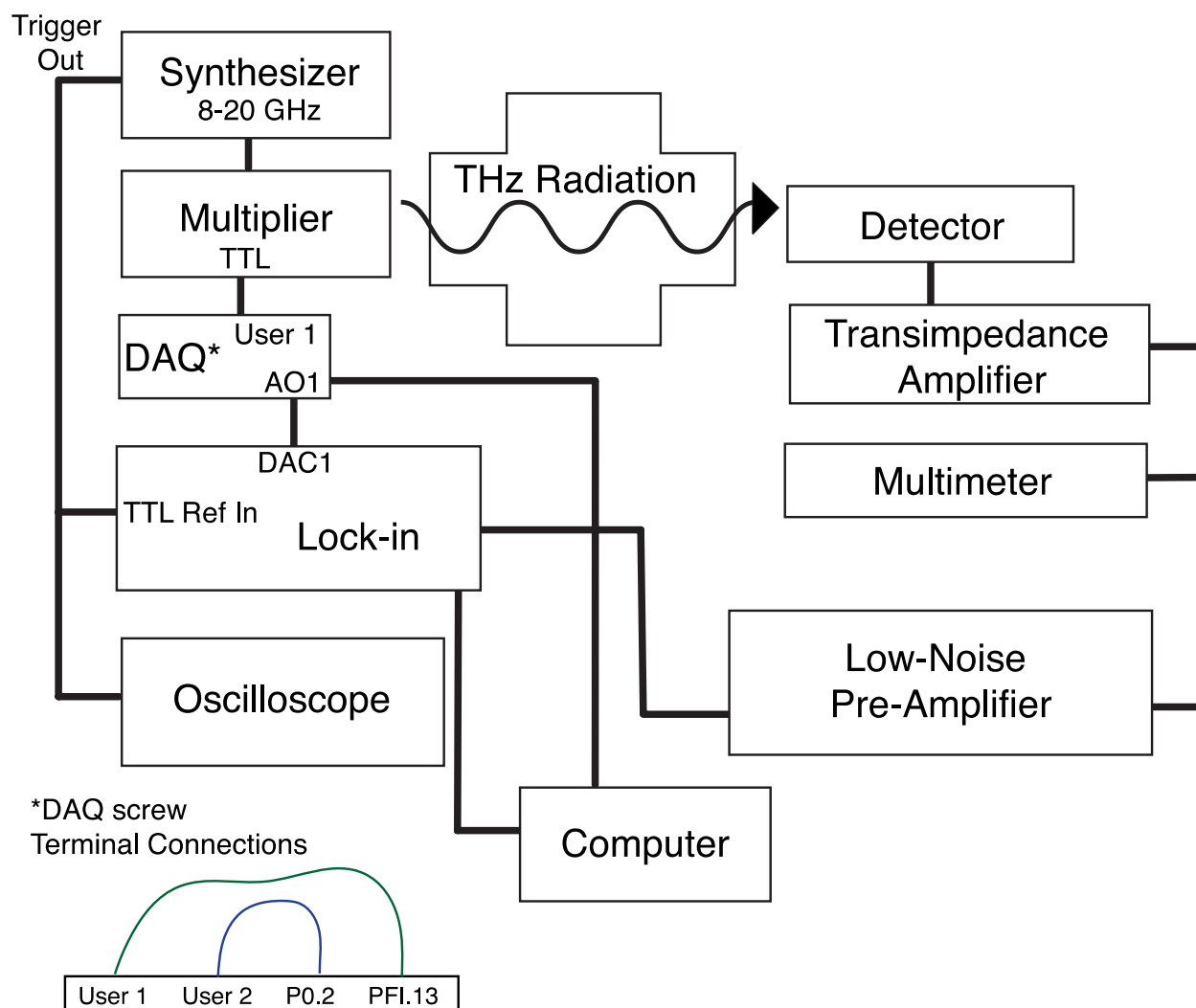


Figure S3. Block diagram the configuration of electronics used during frequency modulated rotational spectroscopy experiments.

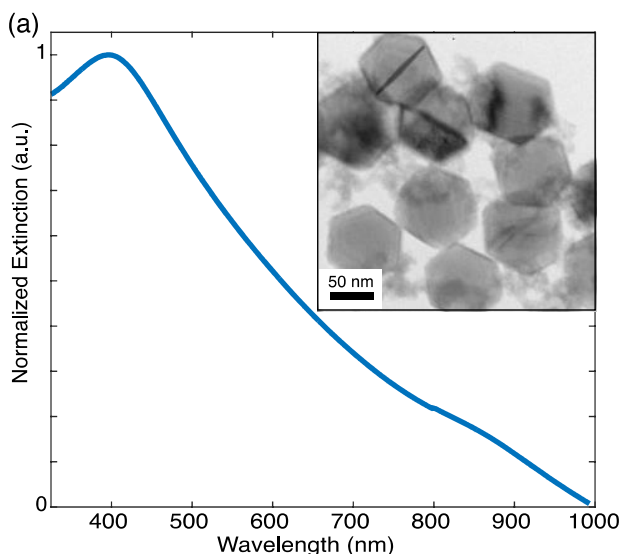


Figure S4. Extinction Spectra of AlNCs used in the main text showing a LSPR at 400 nm. The inset shows a TEM of general nanoparticle morphology; scale bar is 50 nm.

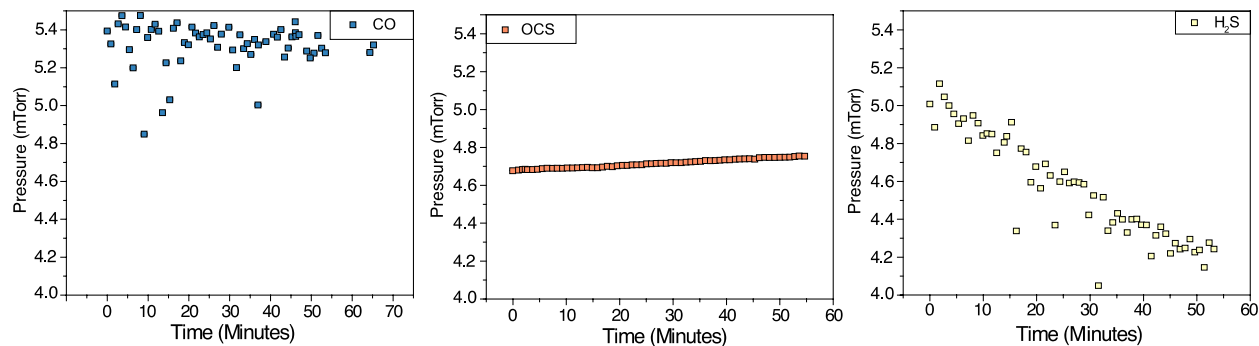


Figure S5. Adsorption of CO, OCS, and H₂S, measured following the separate introduction of ~5 mTorr of each gas to the reaction chamber containing Al NCs on a quartz support. CO (left) does not show any appreciable change over the course of 60 minutes. The OCS pressure (center) increases slightly over the course of 60 minutes, which we attribute to initially over-pressuring the chamber with OCS followed by desorption of excess adsorbed OCS from the chamber/sample. H₂S (right) clearly adsorbs to the chamber walls and/or sample.

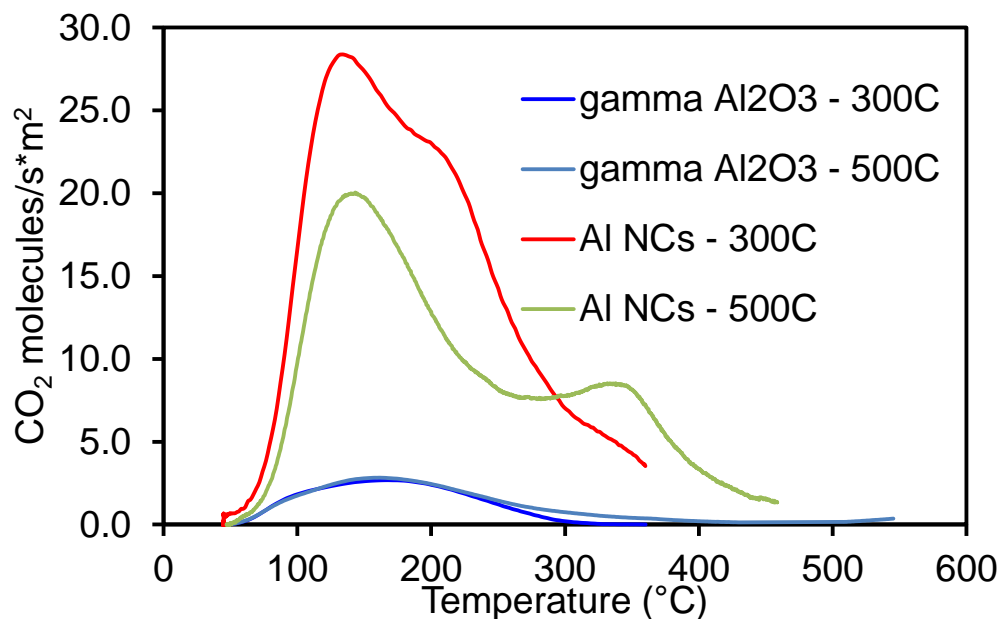


Figure S6. The effect of pretreatment temperature on AlNC basic sites. At 300 °C pretreatment temperatures two distinct desorption events at ~150 °C and a shoulder at ~200 °C are visible on AlNCs. However, when the sample is pretreated at higher temperatures nearing 500 °C, the ~150 °C desorption feature remains prominent, but the shoulder has not shifted to ~350 °C. This suggests that pretreatment of AlNCs can influence surface chemistry. Commercial γ -Al₂O₃ shows no response to pretreatment temperature and approximately an order of magnitude less basic sites.

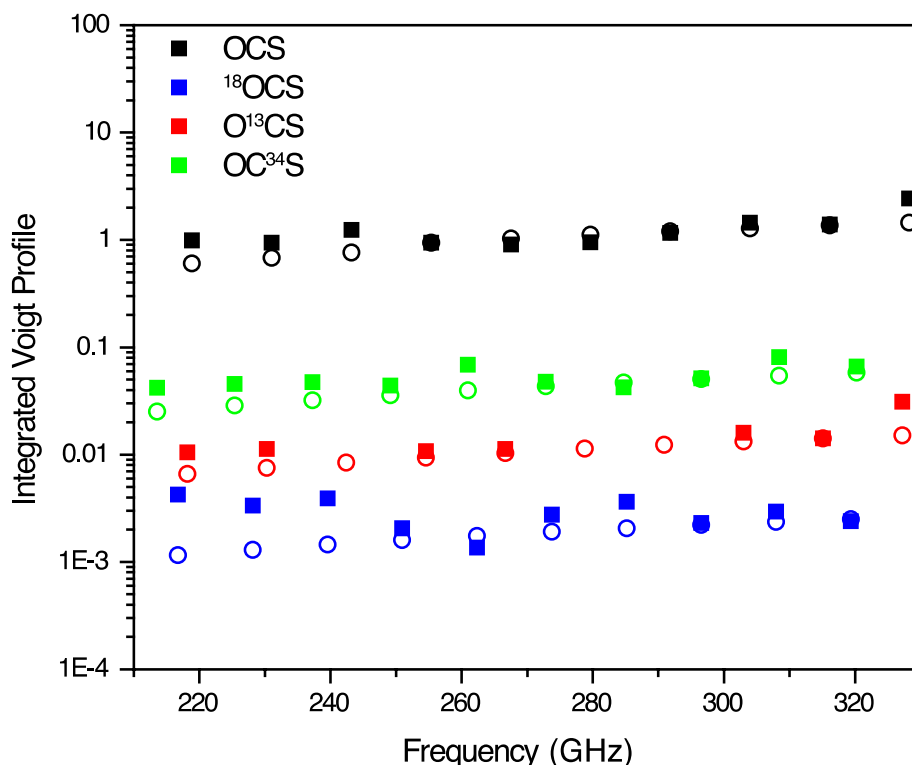


Figure S7. Comparing isotopologues of OCS. Line strengths of four OCS isotopes were measured between 200 - 300 GHz (closed squares) and compared with the predicted line strengths (open circles) using the JPL database and natural abundances (93.7% OCS, 0.19% ^{18}OCS , 1.0% O^{13}CS , and 4.2% OC^{34}S). The average percent error of predicting each isotopic transition using the transition at 255 GHz as the standard was $8.3\% \pm 16.7\%$. These measurements were done at a total pressure of 5.8 mTorr which means the partial pressure of the other species is 11.6 μTorr ^{18}OCS , 58 μTorr O^{13}CS , and 244 μTorr OC^{34}S .

Supplementary References

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- (2) Townes, C. W.; Schlawlow, A. L. *Microwave Spectroscopy*. McGraw Hill, 1955.
- (3) Gordy, W.; Cook, R. L. *Microwave Molecular Spectroscopy*. Wiley-Interscience: New York, 1984.